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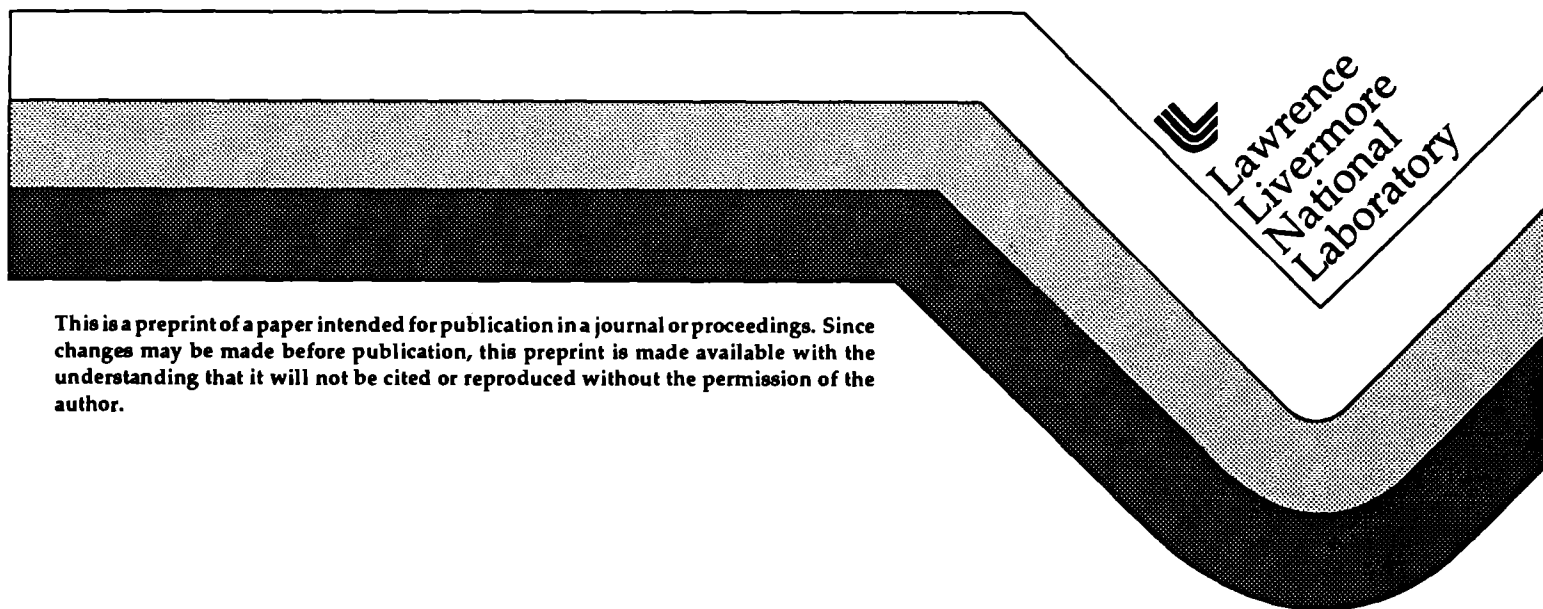
DOC # 219946

**Impact of supersonic and subsonic aircraft on ozone:  
Including heterogeneous chemical reaction mechanisms**

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This paper was prepared for submittal to the proceedings of the  
1992 Quadrennial Ozone Symposium  
Charlottesville, VA, June 4-13, 1992

July 5, 1992



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## ABSTRACT

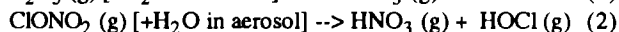
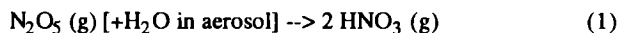
Preliminary calculations suggest that heterogeneous reactions are important in calculating the impact on ozone from emissions of trace gases from aircraft fleets. In this study, three heterogeneous chemical processes that occur on background sulfuric acid aerosols are included and their effects on  $O_3$ ,  $NO_x$ ,  $Cl_x$ ,  $HCl$ ,  $N_2O_5$ ,  $ClONO_2$  are calculated.

## INTRODUCTION

The aircraft industry is showing interest in the development of supersonic, High Speed Civil Transports (HSCT's) for intercontinental passenger flights. The purpose of this study is to extend recent research (Johnston et al., 1989; Weissenstein et al., 1991; Kinnison and Wuebbles, 1991; and Jackman et al., 1991) examining global environmental effects from potential future emissions of commercial aircraft fleets. In addition to the gas-phase reaction mechanism believed to be important in the troposphere and stratosphere, three heterogeneous chemical processes that occur on and within the bulk of sulfuric acid aerosols are investigated. In this study the LLNL two-dimensional zonally averaged chemical-radiative-transport model of the troposphere and stratosphere is used to investigate the effects of  $NO_x$  emissions from future fleets of both subsonic and supersonic aircraft on ozone and other trace gas distributions. Recent uses of this model include those of Johnston et al., 1989 and Wuebbles et al, 1992. For a general description of the LLNL 2-D model, see Kinnison et al., 1992.

## HETEROGENEOUS REACTIONS

In this study, we added the following reactions to the LLNL 2-D model chemistry package:



Since a complete treatment of these reactions would require a sophisticated aerosol microphysical model, which currently has both theoretical and practical limitation, we treated these reactions using the following relationship to calculate the two rate constants for the above cases.

$$K = (V)(\gamma)(\text{Surface Area Density})$$

Surface area density ( $cm^2/cm^3$ ) for the reference atmosphere is based on analysis of Sage II data by Poole, Thomason, and Yue (WMO/UNEP,1992). This distribution is representative of an atmosphere that has not been influenced by a major volcanic eruption. The surface area density distribution has altitude (12-32 km), latitude (90N-90S), and temporal resolution. The effective collision velocity ( $V$ ) is  $5200 \text{ cm/s}$

for this study. The reaction probability per collision ( $\gamma$ ) is based on laboratory measurements (WMO/UNEP,1992). For  $N_2O_5$  on sulfuric acid aerosols the reaction probability ( $\gamma_1$ ) is set to 0.1 and does not have a temperature dependence. The reaction probability for  $ClONO_2$  on sulfuric acid aerosols does have a temperature dependent expression:

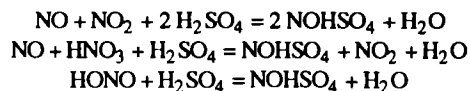
$$\gamma_2 = 0.006 \exp(-0.15(T-200)).$$

In addition, Burley and Johnston (1992), have proposed an additional heterogeneous chemical mechanism. This mechanism has the net effect of converting  $HCl$  into  $ClNO$ . A brief description of the major points about this mechanism are described below. For a more complete description of the modeling approach use in this study, see Connell et al., 1992.

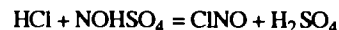
\*Nitrosyl sulfuric acid (NSA) --  $NOHSO_4$  -- has been observed as a solid crystalline precipitate in the stratospheric sulfuric acid aerosol

\*NSA can be present in sulfuric acid solutions where the  $H_2SO_4$  weight per cent is greater than 60 % at typical stratospheric temperatures, either as an ionic solid --  $NO^+HSO_4^-$  -- or as  $H_2ONO^+$  and  $HSO_4^-$  in solution

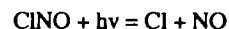
\*Potential NSA formation reactions (Burley and Johnston, 1992) on sulfuric aerosols include:



\* $HCl$  reacts with NSA to form  $ClNO$ :



\*The  $ClNO$  produced is readily photolyzed to form  $Cl$ :

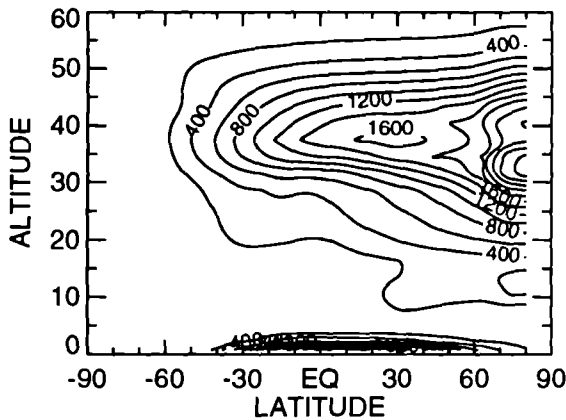


\*The overall process is the acid-catalyzed conversion of the chlorine reservoir species  $HCl$  to active atomic  $Cl$

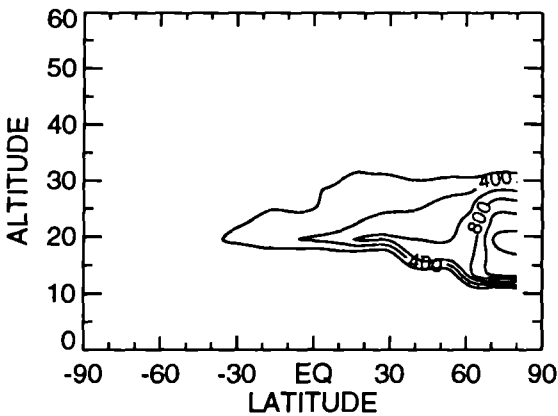
## EMISSION SCENARIO FOR 2015 AIRCRAFT FLEET

Emission scenarios for this study are taken from a recent investigation conducted by the NASA High Speed Research Program (Prather et al, 1992). In these scenarios both subsonic and supersonic aircraft fleets are represented for the year 2015. The trace gas emissions for the 2015 subsonic scenario are based on the Boeing B6 scenario. The subsonic emission scenario was divided into two regions, flights under 400 miles or short range, and flights greater than 400 miles or long range. The total amount of fuel consumed is  $20 \times 10^9$

kg/year and  $150 \times 10^9$  kg/year for short and long range flights respectively. The subsonic emission index for  $\text{NO}_x$  is 20.7 g/kg fuel consumed. The altitude of injection for short range flight is between 6.1 and 9.1 km and between 9.1 and 12.2 km for long range flights. For this study only the Mach 2.4 (16.8-19.8 km) airframe was considered. The total amount of fuel consumed for the supersonic scenario is kept constant at  $70 \times 10^9$  kg/year, which represents approximately 500 aircraft. The supersonic emission index for  $\text{NO}_x$  is 15g/kg fuel consumed. For the above prototype, fuel use during take off, climb, and descent is ignored. In both the subsonic and supersonic emission scenarios, the  $\text{NO}_x$  emitted is 90% NO and 10%  $\text{NO}_2$  on a molecular basis.



**Figure 1:** Rate of reaction of  $\text{HCl} + \text{OH} = \text{Cl} + \text{H}_2\text{O}$  (molec.  $\text{cm}^{-3} \text{s}^{-1}$ ) for an ambient 2015 atmosphere that includes  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  reactions on sulfuric acid aerosols, summer solstice.



**Figure 2:** Rate of reaction of  $\text{HCl} + \text{NSA} = \text{ClNO} (\text{g}) + \text{H}_2\text{SO}_4$  (molec.  $\text{cm}^{-3} \text{s}^{-1}$ ) for an ambient 2015 atmosphere that includes NSA, summer solstice. Contour intervals are: 200, 400, 600... with a maximum of 1200.

### RESULTS

In figure 1, the HCl and OH rate of reaction is shown for the ambient 2015 heterogeneous atmosphere that includes the reactions of  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  on sulfuric acid aerosols. Figure 2 indicates the importance of the NSA mechanisms for converting HCl to reactive chlorine in the lower

stratosphere. Including the NSA mechanism reduces HCl by up to 10-20 percent in the lower stratosphere, increasing the  $\text{ClONO}_2/\text{HCl}$  ratio by 20-30 %;  $\text{Cl}_x$  ( $\text{Cl} + \text{ClO}$ ) and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) change by +50 to +200 % and -4 to +8 % respectively (see Connell et al., 1992 for more details on the impact of NSA on trace gas distributions). As  $\text{NO}_x$  is increased from the proposed aircraft scenario, the NSA concentration will increase which increases the NSA + HCl reaction rate, at high latitudes, Northern Hemisphere, from 1200 to 1800 molecules  $\text{cm}^{-3} \text{s}^{-1}$ . The HCl concentration decreases by another 15 percent in this region.

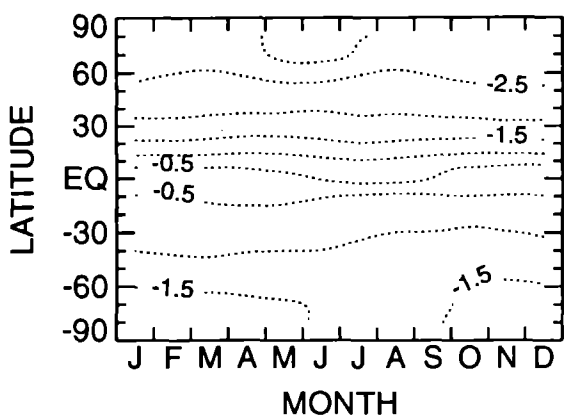
**Table 1:** Percent change in  $\text{ClONO}_2/\text{HCl}$ ,  $\text{Cl}_x$ , and  $\text{NO}_x$  from the Mach 2.4 aircraft fleet emission of  $\text{NO}_x$ , at midlatitudes, in the Northern Hemisphere, July 15.

Chemistry Set	$\text{ClONO}_2/\text{HCl}$	$\text{Cl}_x$	$\text{NO}_x$
Gas-phase	-20 to -30	-50 to -60	+80
Heterogeneous	-4 to -8	-40	+60
Het. with NSA	+20 to +40	-20	+50

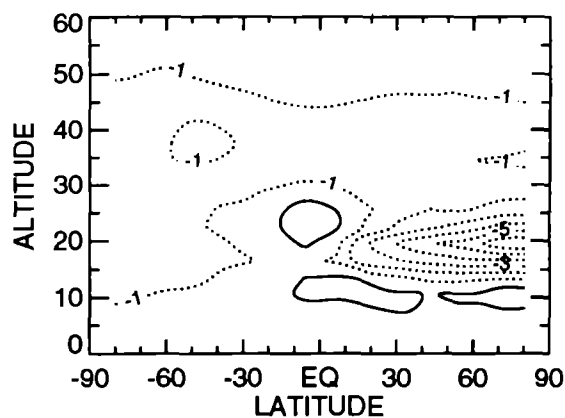
In figure 3, the percent change in column and local ozone is plotted for gas-phase, heterogeneous ( $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  reactions) and heterogeneous ( $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  reactions) with the NSA mechanism. Without the heterogeneous chemical reactions, the  $\text{NO}_x$  emissions decrease global annual-average column ozone by -1.4 %. This decrease is due to the 80 % increase in  $\text{NO}_x$  which increases the rate of odd oxygen loss from the  $\text{NO}_x$  catalytic cycles (table 1). Including both the  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  heterogeneous reactions decreases the effect on ozone of the Mach 2.4 scenario (figures 3b and 3c). The percent global annual-average column ozone change is -0.21 %. With the heterogeneous reactions present, the odd oxygen loss from the  $\text{NO}_x$  catalytic cycles are reduced and the  $\text{Cl}_x$  catalytic cycles are increased. As the emitted  $\text{NO}_x$  reacts with the enhanced  $\text{Cl}_x$  in the heterogeneous atmosphere, the local excess  $\text{NO}_x$  is reduced, minimizing the fleets impact on ozone. When the NSA mechanism is included, the change in global annual-average column ozone is -0.15 %. The net effect of the aircraft  $\text{NO}_x$  emissions is to increase the  $\text{ClONO}_2/\text{HCl}$  ratio, but at least for this Mach 2.4 scenario, did not change ozone concentrations dramatically (compare figures 3c and 3e).

Derived local ozone increases in the troposphere when the heterogeneous reactions are present. This is not observed in the gas-phase case (compare figures 3b with 3d). Since the heterogeneous reactions decrease  $\text{NO}_x$  relative to the gas-phase only mechanism, additional input of  $\text{NO}_x$  is very efficient in producing ozone via the  $\text{CH}_4\text{-NO}_x$ -smog reactions.

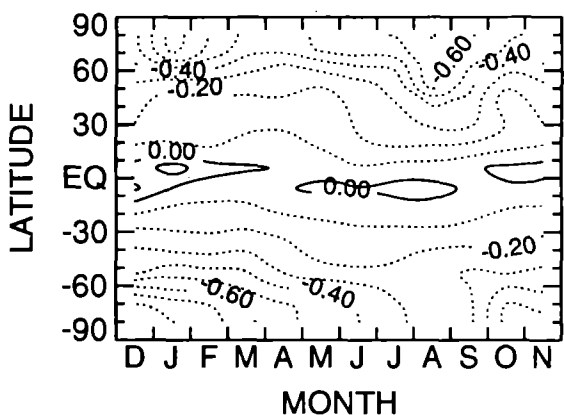
When emissions of the proposed subsonic fleet are included with the Mach 2.4 supersonic fleet, maximum local ozone changes in the troposphere are greater than 10 % for the heterogeneous case without NSA chemistry (figure 4). Approximately 3 percent (see figure 3d) of this change is from supersonic emissions and the rest is due to subsonic emissions. Both the heterogeneous with and without NSA showed similar increases in tropospheric ozone. The global



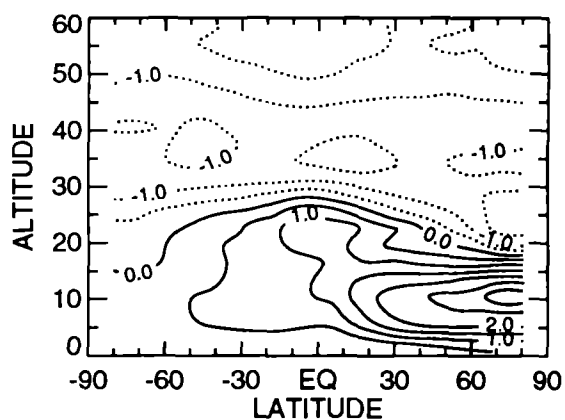
3 a



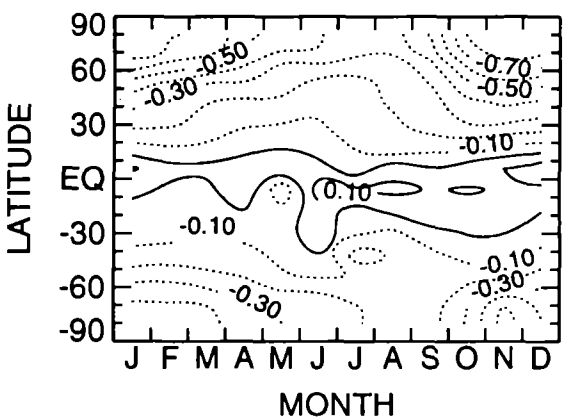
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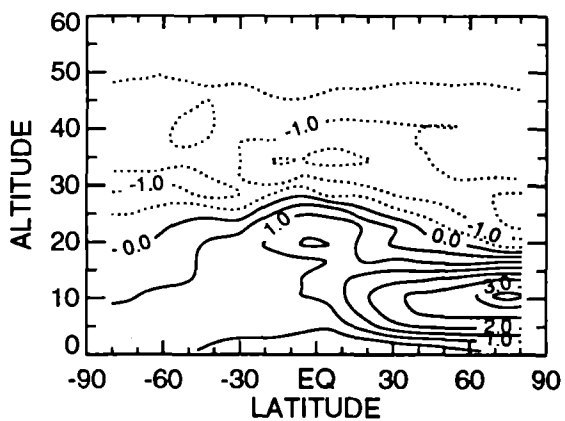
3 c



3 d

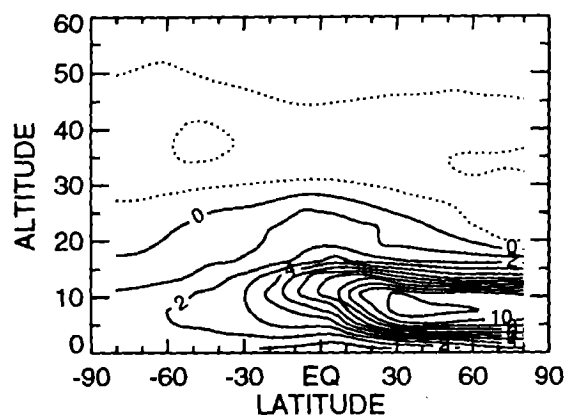


3 e



3 f

**Figure 3:** Percent change in ozone relative to an ambient atmosphere without aircraft for: a) column ozone, gas-phase reaction set; b) local ozone, gas-phase, July 15; c) column ozone, heterogeneous (i.e.,  $N_2O_5$  and  $ClONO_2$  reactions); d) local ozone, heterogeneous, July 15; e) column ozone, heterogeneous with NSA; f) local ozone, heterogeneous with NSA, July 15. There are no subsonic emissions included in these cases.



**Figure 4:** Percent change in local  $O_3$  for an ambient 2015 atmosphere with both proposed subsonic and supersonic emissions of  $NO_x$  from aircraft, July 15. This scenario includes the  $N_2O_5$  and  $ClONO_2$  heterogeneous reactions.

annual-average change in ozone increases by 0.48 % and 0.32 % when both the proposed supersonic and subsonic aircraft fleets are included with and without NSA respectively.

## CONCLUSIONS

- 1) The rate of  $OH + NSA$  is comparable to  $OH + HCl$  in the lower stratosphere (Figures 1 and 2).
- 2) With the gas-phase only chemistry mechanism, relatively large changes ( $> 3\%$  column ozone change at high latitudes in the northern hemisphere) occur when the  $NO_x$  emissions from the proposed Mach 2.4 fleet are modeled (Figures 3a and 3b).
- 3) Including  $N_2O_5$  and  $ClONO_2$  reactions on sulfuric acid aerosols decreases the ozone loss relative to what was derived with a gas-phase only chemical mechanism (Figures 3c and 3d).
- 4) Including NSA chemistry with the  $N_2O_5$  and  $ClONO_2$  reactions does not change the net ozone production or loss from the aircraft scenario by a large amount from that derived with the  $N_2O_5$  and  $ClONO_2$  chemistry only case (Figures 3e and 3f).
- 5) When the heterogeneous reactions are included, there is a net increase in ozone in the troposphere. This is not observed with the gas-phase only case (compare figures 3b with 3d).
- 6) When subsonic emissions are included with the proposed HSCT fleet, large positive changes in tropospheric ozone are derived (Figure 4).

## ACKNOWLEDGMENTS

The authors would like to thank Chi Tang for her contributions in analyzing and plotting the results for this study. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48 and was supported in part by the NASA High Speed Research Program.

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